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(54) **Hydrotreating process.**

(57) Process for hydrotreating a hydrocarbon oil employing several reactor vessels, which process comprises :

(i) further hydrotreating partly hydrotreated hydrocarbon oil (8) of step (iv) in a first reactor vessel (1) in the presence of clean hydrogen containing gas (1),

(ii) separating (3) the mixture obtained in step (i) within the first reactor vessel into a hydrotreated hydrocarbon oil (4) and used hydrogen containing gas (3), which hydrotreated hydrocarbon oil can be recovered as product,

(iii) hydrotreating fresh hydrocarbon oil (5) in the second reactor (2) vessel in the presence of used hydrogen containing gas (3) obtained in step (ii),

(iv) separating the effluent of step (iii) into partly hydrotreated hydrocarbon oil (8) and contaminated hydrogen containing gas (7), and

(v) transporting partly hydrotreated hydrocarbon oil obtained in step (iv) to step (i).

EP 0 611 816 A1

The present invention relates to a process for hydrotreating a hydrocarbon oil employing at least a first and a second reactor vessel.

It is foreseen that the amount of contaminating compounds such as sulphur or nitrogen containing compounds and aromatics, which are allowed to be present in hydrocarbon oils according to environmental regulations, will continuously decrease in the future. Therefore, there is much interest in processes with the help of which the amount of these compounds contained in hydrocarbon oils can be brought to a low level in a commercially attractive way.

Processes for reducing the amount of sulphur or nitrogen containing compounds and aromatics, are in general called hydrotreating processes. These processes can be further divided into processes which are especially directed at saturation of unsaturated compounds such as aromatics and olefins, in which case they are called hydrogenation processes, and processes which are especially directed at reducing the amount of sulphur containing compounds and often at the same time also of nitrogen containing compounds, in which case they are called hydrodesulphurization processes. There are also processes which are specifically directed at reducing the amount of nitrogen containing compounds and in which only a relatively small amount of sulphur containing compounds are removed. These are called hydrodenitrogenation processes. With the expression hydrodesulphurization processes, which is used hereinafter, processes are meant which are either directed at removal of sulphur containing compounds and optionally a limited amount of nitrogen, or processes which are primarily directed at removal of nitrogen containing compounds and in which further some sulphur containing compounds are removed.

A large variety of hydrotreating processes are known from the prior art, for instance from US patent specification 5,114,562. In this document a process for hydrotreating a middle distillate has been described. The process comprises hydrodesulphurization of the distillate, cooling the effluent obtained and subsequently stripping it to remove hydrogen sulphide. The vapour phase portion from the stripping section is further cooled and thereafter further separated in a low pressure vapour-liquid separation zone. The stripped liquid fraction is hydrogenated. The effluent of the hydrogenation zone is removed from the reactor, cooled several times, and subsequently separated into a liquid phase stream and a vapour phase stream. The liquid phase stream is removed and further separated into several product fractions employing a product recovery fractionation means. It is mentioned that this set-up makes that only a single gas compressor is needed for the gas recycle loop.

The aim of the present invention is improvement in the economics of a hydrotreating process. This is attained by integration of the means for separating the effluent of the final hydrotreating step into the reaction vessel in which this final hydrotreating step is carried out. This makes that one of the separation vessels can be dispensed with. As the separation vessels which are applied in this kind of processes must be able to withstand quite high temperatures and pressures, it is advantageous to be able to dispense with one of them. Further, in the present set-up it is possible to more easily maintain the temperature of the used hydrogen containing gas which is applied in the further hydrotreatment. This makes that in certain cases reheating of the gas can be avoided.

The present invention relates to a process for hydrotreating a hydrocarbon oil employing at least a first and a second reactor vessel, which process comprises:

(i) contacting partly hydrotreated hydrocarbon oil obtained in step (iv) described hereinbelow, in the first reactor vessel at elevated temperature and pressure with a hydrotreating catalyst in the presence of clean hydrogen containing gas,

(ii) separating the mixture obtained in step (i) within the first reactor vessel into a hydrotreated hydrocarbon oil and used hydrogen containing gas, which hydrotreated hydrocarbon oil can be recovered as product,

(iii) contacting fresh hydrocarbon oil in the second reactor vessel at elevated temperature and pressure with a hydrotreating catalyst in the presence of used hydrogen containing gas obtained in step (ii),

(iv) separating the effluent of step (iii) into partly hydrotreated hydrocarbon oil and contaminated hydrogen containing gas, and

(v) transporting partly hydrotreated hydrocarbon oil obtained in step (iv) to step (i).

In order to be able to separate the mixture obtained in step (i) to a sufficient extent into liquid hydrocarbon oil and hydrogen containing gas inside the reactor vessel, the hydrocarbon oil which is to be subjected to the present process is to be such that the partly hydrotreated hydrocarbon oil which is processed in step (i) contains a substantial amount of hydrocarbons which are liquid at the process conditions prevailing in the first reactor vessel. It is possible to cool the part of the reactor vessel in which the separation is carried out, such that it would also be possible to process feeds of which a relatively small percentage is in the liquid phase at the process conditions which prevail in the part of the first reactor vessel in which the hydrocarbons are converted. However, this is not a preferred embodiment. In general, the separation of step (ii) will be carried out at a temperature and a pressure which are substantially the same as the temperature and pressure applied in step (i).

The separation inside the first reactor vessel can be carried out in any suitable way. An option could be

cooling as described above, with subsequent separate removal of the gaseous components and liquid components. However, other separation methods are preferred. A suitable method involves the use of a separation means comprising a downwardly extending plate having an opening between the lower edge of the plate and the wall of the vessel, at which lower edge there is a downwardly extending flange. The opening between the lower part of the plate and the wall of the vessel should be such that it allows gas and liquid to flow freely through it. Further, the surface of the plate in proportion to the vessel cross section is to be such that it sufficiently reduces the gas velocity, while the flange is to generate centrifugal effects which promote gas/liquid separation. The gas is preferably removed at a place which is just below the upper part of the plate, while the liquid is preferably removed at the lowest part of the reactor vessel. Such separation means has been depicted in Figure 1 (number (3)) and Figure 2 (number (23)).

In general it will be advantageous to process a hydrocarbon oil of which a major amount, for example more than 70 % by weight, suitably more than 80 % by weight and preferably more than 90 % by weight, is in the liquid phase at the process conditions prevailing in the first reactor vessel. Hydrocarbon oils which can suitably be hydrotreated according to the present invention, are kerosene fractions, gas oil fractions and lubricating oils. Especially a gas oil fraction can very suitably be subjected to the present invention, as the environmental constraints on gas oils are tightening. A suitable gas oil would be one of which a major portion of the hydrocarbons, e.g. at least 75 % by weight boils in the range of between 150 and 400 °C. A suitable lubricating oil contains at least 95% by weight of hydrocarbons boiling in the range of between 320 and 600 °C.

A hydrotreating catalyst which can be employed in the process according to the present invention suitably comprises one or more metals from Group IB, IIA, IVB, VB, VIB and VIII of the Periodic Table of the Elements in the Handbook of Chemistry and Physics, 63rd edition, on a solid carrier. The carrier can comprise any metal oxide or mixed metal oxide support. Suitable supports comprise amorphous silica, amorphous alumina, amorphous silica-alumina, and zeolite with silica or alumina as a binder.

The separation in step (iv) will often be carried out at a temperature which is lower than the temperature at which the hydrotreating of step (iii) is carried out. This is done as the hydrotreatment of step (iii) is usually carried out at higher temperature than the hydrotreatment of step (i), because the hydrotreatment of step (iii) is usually to be carried out at higher severity. This makes that for some feedstocks it is possible to attain sufficient separation substantially at process conditions in step (ii), while this is not possible in step (iv). The pressure applied in step (iv) is preferably substantially the same as the pressure applied in step (iii). In that way the duty of the recycle compressor can be minimised. The separation can be carried out in any way known to be suitable to someone skilled in the art, for example with the help of a so called high pressure separator. This would make that only one gas pump would be needed for maintaining the recycle flow of the hydrogen containing gas. This makes that good hydrotreating results are obtained in a commercially attractive way. It is even more preferred to carry out the separation at substantially the same pressure as applied in step (iii) and with the help of a stripper. Such stripper will usually contain a stripping column in the upper part of which partly hydrotreated hydrocarbon oil is introduced, and in the lower part of which stripping gas containing hydrogen is introduced. The stripped liquid is removed at the bottom and the stripping gas is removed at the top. In this way, a substantial amount of the hydrogen sulphide present in the hydrocarbon oil is removed. This is advantageous for the final hydrotreatment step, which gives better results if less hydrogen sulphide is present.

With the expression "clean hydrogen containing gas" is meant a gas containing less than 3% by volume of hydrogen sulphide, preferably less than 1% by volume, more preferably less than 0.5% by volume, most preferably less than 0.1% by volume. Suitably, contaminated hydrogen containing gas obtained in step (iv) is cleaned, e.g. by treating it with an amine, and subsequently used again in step (i) as clean hydrogen containing gas.

In principle, the flow in the conversion zones of the reactor vessels can be upwards or downwards. However, it is preferred to pass the hydrogen containing gas and the hydrocarbon oil through the reactor vessels cocurrently in downflow. In this way, the gas flow and liquid flow can be controlled in an operationally reliable way. Further, the reactor temperatures can more easily be reliably controlled.

As mentioned before, hydrotreating processes can be divided in hydrogenation and hydrodesulphurization processes. The process according to the present invention suitably comprises a hydrodesulphurization process in step (iii) followed by a further hydrodesulphurization process in step (i). In this way, a very low sulphur level can be attained in a commercially attractive way. Another possible combination of processes comprises hydrodesulphurization of a hydrocarbon oil, more specifically a gas oil, in step (iii) followed by hydrodesulphurization in step (i). In both of these processes a hydrodesulphurization catalyst could be applied. However, the conditions and catalyst of the hydrodesulphurization of step (i) will usually be selected such it is more directed at aromatics saturation. A further embodiment of the present invention comprises a hydrodesulphurization process in step (iii) followed by a hydrogenation process in

step (i). In this embodiment both the sulphur and the aromatics content of the fresh hydrocarbon oil can be diminished in a commercially attractive way. It has been found that this combination of processes is especially suitably applied in the present invention. It should be noted that the expression hydrodesulphurization processes, is used for referring to processes primarily directed at removal of sulphur containing compounds and processes which are specifically directed at removal of nitrogen containing compounds and in which also a certain amount of sulphur containing compounds is removed.

If the process according to the present invention comprises in step (i) a hydrogenation process and in step (iii) a hydrodesulphurization process, in step (i) a hydrogenation catalyst will usually be applied at hydrogenation conditions, and in step (iii) a hydrodesulphurization catalyst will be applied at hydrodesulphurization conditions. In such case, the hydrodesulphurization of step (iii) must in general be carried out such that a sulphur content is attained which meets the specification on the sulphur tolerance of the hydrogenation catalyst of step (i). Otherwise, this hydrogenation catalyst would be poisoned. Suitably, the hydrocarbon oil obtained in step (iv) contains not more than 15% by volume of sulphur containing compounds, based on the volume of sulphur containing compounds present in the fresh hydrocarbon oil, preferably not more than 10%. The catalysts to be used can in principle be any commercially available hydrogenation and hydrodesulphurization catalyst. In general such catalyst will comprise one or more Group VIB metals and/or one or more Group VIII metals. A hydrogenation catalyst which is especially suitable for use in step (i) comprises as catalytically active metal one or more metals from the group formed by platinum, palladium, tungsten, molybdenum, nickel and cobalt, on a solid carrier.

If the process according to the present invention comprises in both steps (i) and (iii) a hydrodesulphurization process, a hydrodesulphurization catalyst will in these steps be applied at hydrodesulphurization conditions. In that case, the partly hydrotreated hydrocarbon oil obtained in step (iv) suitably contains between 0.01% and 30% by volume of sulphur containing compounds, based on the volume of sulphur containing compounds present in the fresh hydrocarbon oil. Any hydrodesulphurization catalyst can be used. Suitably, catalysts are used containing one or more metals from Group IB, IIA, IVB, VB, VIB and VIII of the Periodic Table of the Elements on a solid carrier. A preferred catalyst comprises nickel, molybdenum, cobalt and/or tungsten, on a solid carrier. The catalysts of step (i) and (iii) can be different, or the same.

If a gas oil is hydrotreated in the process according to the present invention, steps (i) and (iii) are suitably carried out at a temperature of between 150 and 450 °C, suitably between 250 and 400 °C, preferably between 300 and 390 °C, more preferably between 310 and 385 °C, and a pressure of between 15 and 150 bar, preferably between 25 and 120 bar. A suitable gas oil would be one as described above, which contains at least 75% by weight of hydrocarbons boiling in the range of between 150 and 400 °C.

If a lubricating oil is hydrotreated in the process according to the present invention, steps (i) and (iii) are suitably carried out at a temperature of between 150 and 400 °C, preferably between 250 and 390 °C, more preferably between 310 and 385 °C, and a pressure of less than 250 bar, preferably less than 200 bar, more preferably less than 175 bar. A suitable lubricating oil would be one as described above, of which more than 95% by weight, boils in the range between 320 and 600 °C.

The process according to the present invention is to be carried out in at least two reactor vessels. It is of course possible to use more vessels, for example by carrying out the process of step (i) and/or (iii) in more than one reactor vessel. This could for example be done for throughputs which are too large for carrying out such process step in a single reactor vessel. If process step (i) is carried out in more than one reactor vessel, the separation within the vessel (step (ii)) can be carried out solely in the last vessel of this process step.

The hydrotreated hydrocarbon oil which is produced in the present process can be further processed in any conventional way. Suitably, the product will be sent to a fractionator to obtain several product fractions, such as a lubricating oil, a diesel fuel, a jet fuel, etc.

A possible embodiment of the process according to the present invention has been shown schematically in Figure 1 for illustration. In Figure 2 a more detailed possible process scheme has been given.

The first and second reactor vessel ((1) and (2)) of Figure 1 both contain a suitable hydrotreating catalyst. Clean hydrogen containing gas of line 1, is mixed with partly hydrotreated hydrocarbon oil of line 8, and the mixture is introduced via line 2 into the first reactor vessel (1). The mixture is contacted with the catalyst at elevated temperature and pressure, and the effluent obtained is separated within the vessel employing a separation means (3) consisting of a downwardly extending plate at which lower end there is a downwardly extending flange, as described above. The hydrotreated hydrocarbon oil which is obtained, can be recovered as product via line 4. The used hydrogen containing gas is led via line 3 to the second hydrotreating reactor. The used hydrogen containing gas is mixed with fresh hydrocarbon oil of line 5, and the mixture is introduced in the second reactor vessel (2). In this reactor vessel, the mixture is contacted at elevated temperature and pressure with the hydrotreating catalyst. The effluent obtained is

led via line 6 and preferably after cooling, to high pressure separator (4). In this vessel the contaminated hydrogen containing gas is separated off and removed via line 7. The partly hydrotreated oil obtained is transported via line 8 to the first reactor vessel (1). The contaminated hydrogen containing gas which is separated off, cleaned and subsequently recycled to the process to be used as fresh hydrogen containing gas.

A more detailed possible process scheme has been depicted in Figure 2. In this scheme, the flow of hydrocarbon oil is followed for describing the scheme. Reactors R1 and R2 contain suitable hydrotreating catalysts. The fresh hydrocarbon oil of line 10 is heated with the help of a furnace (21) and brought at elevated pressure. After having been mixed with used hydrogen containing gas of line 17, which is discussed hereinafter, the mixture of hydrocarbon oil and hydrogen is introduced into reactor R1. In this reactor vessel, the mixture is contacted at elevated temperature and pressure with the hydrotreating catalyst. The effluent obtained is used for heating the mixture of hydrogen and partly hydrotreated oil of line 16 to be discussed hereinafter. The effluent is subsequently sent via line 11 to a stripper (22). To this stripper fresh make-up hydrogen is added via line 12. The contaminated hydrogen containing gas from the stripper (22) is sent via line 13 to unit (25) where it is cleaned by amine scrubbing. The clean hydrogen containing gas of line 15 which is produced, is mixed with the partly hydrotreated hydrocarbon oil from the stripper of line 14. This mixture of line 16 is heated by being indirectly contacted with the effluent of line 11 and subsequently introduced into reactor R2. In this reactor vessel, the mixture is contacted at elevated temperature and pressure with the hydrotreating catalyst. The mixture obtained is separated inside reactor R2 with a downwardly extending plate (23) as described in above. The used hydrogen containing gas is separated off and is passed via line 17 to the fresh hydrocarbon oil of line 10, with which it is mixed. The hydrotreated hydrocarbon oil is sent via line 18 to a stripper (24). The stripped, hydrotreated hydrocarbon oil obtained is sent via line 19 to a separator (26) where it can be further separated into several fractions. The further units which are depicted are part of a conventional work-up section.

Claims

1. Process for hydrotreating a hydrocarbon oil employing at least a first and a second reactor vessel, which process comprises:
   (i) contacting partly hydrotreated hydrocarbon oil obtained in step (iv) described hereinbelow, in the first reactor vessel at elevated temperature and pressure with a hydrotreating catalyst in the presence of clean hydrogen containing gas,
   (ii) separating the mixture obtained in step (i) within the first reactor vessel into a hydrotreated hydrocarbon oil and used hydrogen containing gas, which hydrotreated hydrocarbon oil can be recovered as product,
   (iii)contacting fresh hydrocarbon oil in the second reactor vessel at elevated temperature and pressure with a hydrotreating catalyst in the presence of used hydrogen containing gas obtained in step (ii),
   (iv) separating the effluent of step (iii) into partly hydrotreated hydrocarbon oil and contaminated hydrogen containing gas, and
   (v) transporting partly hydrotreated hydrocarbon oil obtained in step (iv) to step (i).

2. Process according to claim 1, in which the separation of step (ii) is carried out at a temperature and pressure which are substantially the same as the temperature and pressure applied in step (i).

3. Process according to claim 1 or 2, in which the separation of step (iv) is carried out at a pressure which is substantially the same as the pressure applied in step (iii).

4. Process according to claim 3, in which the separation of step (iv) is carried out with the help of a stripper.

5. Process according to any one of claims 1 to 4, in which contaminated hydrogen containing gas obtained in step (iv) is cleaned and used again in step (i).

6. Process according to claim 5, in which the contaminated hydrogen containing gas is cleaned by treating with an amine.

7. Process according to claim 6, in which the clean hydrogen containing gas contains less than 1% by volume of hydrogen sulphide.

8. Process according to any one of claims 1 to 7, in which the hydrocarbon oil to be hydrotreated is a gas oil which contains at least 75% by weight of hydrocarbons boiling in the range of between 150 and 400 °C.

9. Process according to claim 8, in which steps (i) and (iii) are carried out at a temperature of between 150 and 450 °C and a pressure of between 15 and 150 bar.

10. Process according to any one of claims 1 to 7, in which the hydrocarbon oil to be hydrotreated is a

lubricating oil which contains at least 95% by weight of hydrocarbons boiling in the range of between 320 and 600 °C.

11. Process according to claim 10, in which steps (i) and (iii) are carried out at pressure of less than 250 bar and at a temperature of between 150 and 400 °C.

12. Process according to any one of claims 1-11, in which the hydrotreating catalyst comprises one or more metals from Group IB, IIA, IVB, VB, VIB and VIII of the Periodic Table of the Elements, on a solid carrier.

13. Process according to any one of claims 1 to 12, in which in step (i) a hydrogenation catalyst is applied at hydrogenation conditions, and in step (iii) a hydrodesulphurization catalyst is applied at hydrodesulphurization conditions.

14. Process according to claim 13, in which the hydrocarbon oil obtained in step (iv) contains not more than 15% by volume of sulphur containing compounds, based on the volume of sulphur containing compounds present in the fresh hydrocarbon oil.

15. Process according to claim 13 or 14, in which the hydrogenation catalyst used in step (i) comprises as catalytically active metal one or more metals from the group formed by platinum, palladium, tungsten, molybdenum, nickel and cobalt, on a solid carrier.

16. Process according to any one of claims 1 to 12, in which in steps (i) and (iii) a hydrodesulphurization catalyst is applied at hydrodesulphurization conditions.

17. Process according to claim 16, in which the hydrocarbon oil obtained in step (iv) contains between 0.01 and 30% by volume of sulphur containing compounds, based on the volume of sulphur containing compounds present in the fresh hydrocarbon oil.

18. Hydrocarbons whenever obtained in a process as described in any one of the preceding claims.

FIG.1

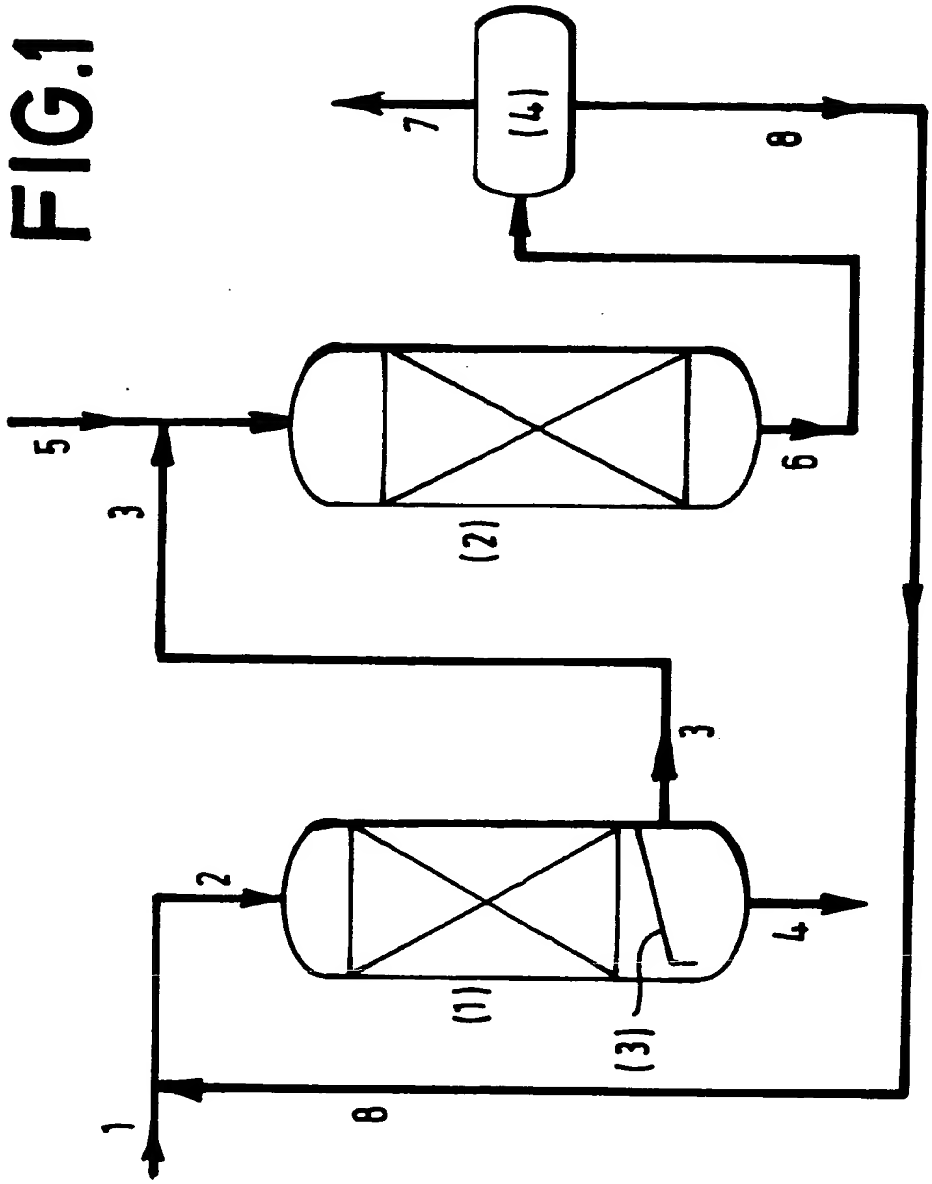
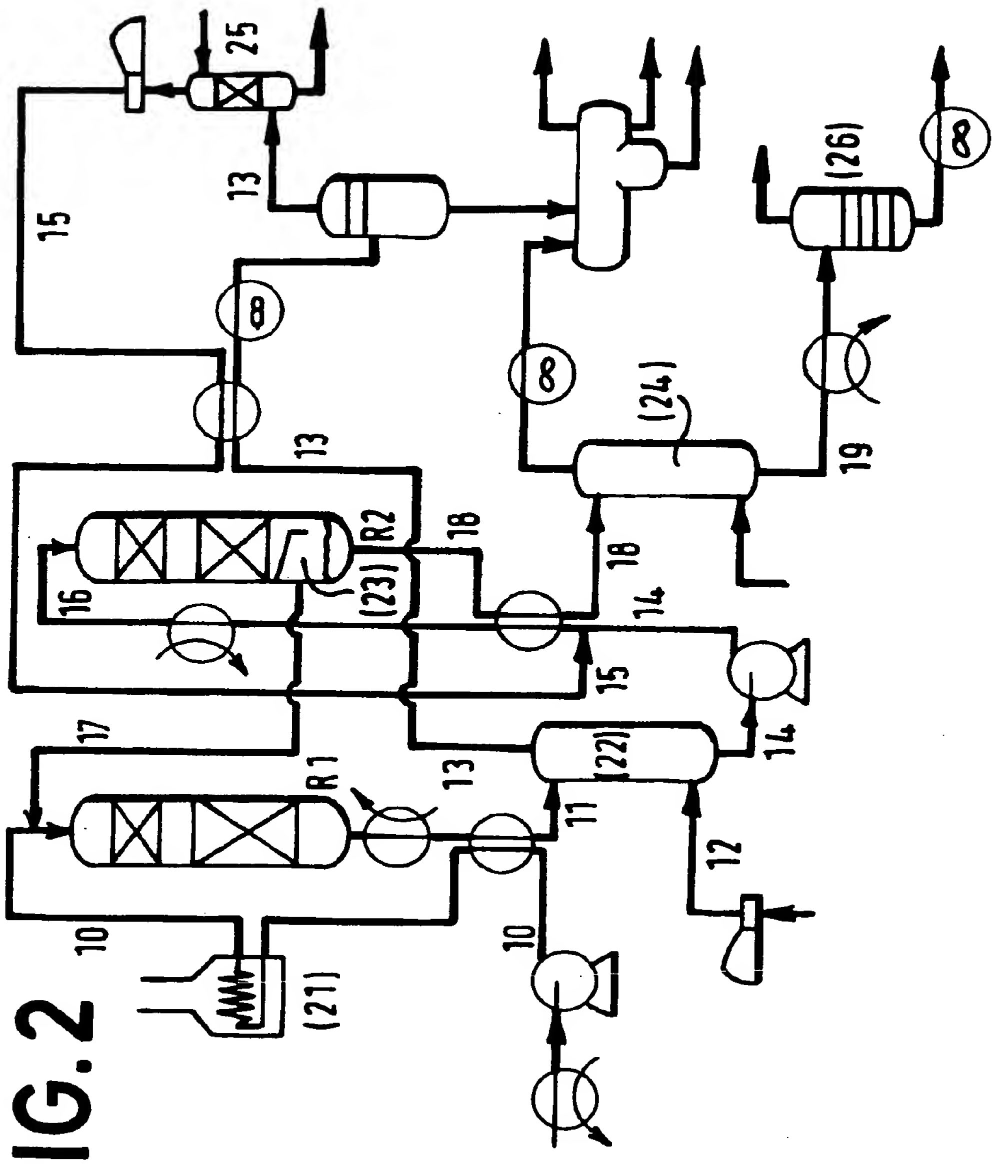


FIG. 2



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EUROPEAN SEARCH REPORT

Application Number
EP 94 20 0372

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	FR-A-2 184 684 (UOP) * the whole document * ---	1-9,12, 16-18	C10G65/04 C10G65/08
X	GB-A-960 440 (ESSO) * the whole document * ---	1-4,8-18	
X	BE-A-571 792 (ESSO) * claims 1-5; figure 2 * ---	1-9, 12-15	
A	US-A-3 915 841 (GULF) * the whole document * -----	10,11	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 May 1994	Michiels, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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